PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :	A1	(11) International Publication Number: WO 93/10652
H05K 3/38		(43) International Publication Date: 27 May 1993 (27.05.93)

(21) International Application Number: PCT/US91/08777

(22) International Filing Date: 22 November 1991 (22.11.91)

(71) Applicant *(for all designated States except US)*: ELECTRO-CHEMICALS, INC. [US/US]; 751 Elm Street, Youngstown, OH (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : HARRYHILL, Therese, M. [US/US]; 514 Ann Street, Niles, OH 44446 (US). MARASOVICH, Gary, M. [US/US]; 2762 Spitler Road, Poland, OH 44514 (US). BURGER, Lee [US/US]; 8475 S. Pricetown Road, Berlin Center, OH 44401 (US). CZAJA, James [US/US]; 13931 Lawn Dale Lane, Dayton, MN 55327 (US).

(74) Agent: POCHOPIEN, Donald, J.; McAndrews, Held & Mallow, Ltd., Northwestern Atrium Center, 500 West Madison Street, Chicago, IL 60661 (US).

(81) Designated States: CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, NL, SE).

Published
With international search report.

(54) Title: PROCESS FOR IMPROVED ADHESION BETWEEN A METALLIC OXIDE AND A POLYMER SURFACE

(57) Abstract

This invention is directed to a process for bonding a layer of copper or a copper alloy to a layer of polymeric material, the process comprising the steps of: (a) oxidizing the surface of a layer of copper or copper alloys with an oxidizing solution to form an oxide coating on the surface; (b) subjecting the oxide coating on the layer of copper or copper alloy to an acidic solution to remove an amount of the oxide coating effective to enhance bonding with a polymeric material, the acidic solution characterized by a pH of between 3.0 to 5.5, more preferably between 3.0 to 4.0; and (c) bonding the layer of copper or copper alloy from step (b) to a polymeric material.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

PROCESS FOR IMPROVED ADHESION BETWEEN A METALLIC OXIDE AND A POLYMER SURFACE

BACKGROUND OF THE INVENTION

The present invention is directed to an improved method for bonding a layer of copper or a copper alloy, via its oxide coating, to a polymeric material. The present invention is useful because it provides an improved method that has applicability in the manufacture of multi-layer electronic circuit boards.

In many manufacturing processes, a polymeric material is bonded to a metallic surface. Prior to the bonding operation, the metallic surface is cleaned, removing oils, grease, oxidation, and/or objectional metals. The cleaned surface is then treated with an alkaline, oxidizing solution. The surface metal is oxidized to a metallic oxide, providing a substrate with a roughened topography. The roughened topography of the oxidized metal has an increased surface area. The increased surface area increases the bond strength between the metal and the polymer. The metal, with the oxide coating, is dried in an oven or a vacuum to remove any surface bound water or gases. The polymer is then bonded to the degassed and dried metal.

The metallic oxide may take the form of "whiskers" or hairlike projections that can be susceptible to fracture when subjected to mechanical disturbance such as may be encountered during drilling or routing operations, or thermal disturbance, such as may be encountered during lamination and soldering. Exposed oxide tends to dissolve during treatment with strong acid cleaning solutions, such as are routinely necessary to prepare laminated boards for plating.

Contemporary multilayer printed circuit board manufacturing incorporates the bonding of layers of polymeric, dielectric prepreg to layers of metallic conductor that have been surfaced with a metallic oxide coating. The metallic conductors are

configured, through processes including photo-etching, to form a pattern having utility as a part of an electrical circuit, thereby avoiding the use of wire connections. Prepregs are a fabric matrix, such as a sheet of glass fibers that have been impregnated with polymeric resins. After a laminate of several layers of copper conductor and dielectric prepreg has been built up, the layers are perforated by a pattern of through holes, usually by drilling.

The surfaces exposed by drilling are cleaned of resin and fiber fragments resulting from the drilling process. They are then coated with a layer of conductive metal to provide electrical connection between the metallic layers exposed by drilling. Oxide failure or fracture can occur during the drilling operation. In the subsequent process steps, the drilled multilayer circuit board is immersed in cleaning and plating solutions, including strong acids. A portion of the oxide coating may dissolve during cleaning and plating, resulting in a visible "pink ring" of bright copper surrounding the hole. The appearance of pink ring is not only unsightly, it may indicate fracture between the dielectric and the copper, resulting in reduced useful life of the circuit, or may be evidence that electrical continuity between the plated surface of the drilled hole, and the laminated metallic conductor has been impaired, in which case the circuit may be defective. In short, the appearance of pink ring is an indication that the adhesion of the laminate, the conducting properties of the circuit, and the insulating properties of the dielectric have been compromised. If this effects the performance of the circuit board, the entire package is discarded, resulting in lost material and labor.

Many attempts have been made to minimize the frequency and the magnitude of the pink ring defect,

by optimizing the bonding, drilling, cleaning, and plating processes. However, as the density of the precise pattern of holes, and the number of layers are increased to produce more compact circuit boards, the formation of pink ring as a consequence of processing continues to be a problem. Therefore, efforts have been directed towards altering the chemical and mechanical attributes of the metallic surface prior to the bonding or laminating step. Such efforts are herein characterized as pre-lamination surface treatments. Those involving altering a brown or black copper oxide layer after an alkaline oxide treatment, are herein characterized as post-oxide treatments.

Several different approaches to post-oxide treatments are claimed to reduce pink-ring problems. One such approach is set forth in U.S. Patent No. 4,643,793, which is incorporated herein by reference. This patent describes a two-step process resulting in a coloring that tends to mask visible pink ring. In the '793 patent, a nitrogen-containing compound capable of forming an electroless deposition of copper retains the dark color imparted by the copper oxide to avoid the appearance of a pink ring.

Another post-oxide approach to the pink ring problem is taught in U.S. Patent No. 4,775,444, which is incorporated herein by reference. The '444 patent describes treating the copper oxide with either aqueous chromic acid, or acidifying an aqueous solution of an alkali metal chromate with a mineral acid to a pH of between 1.5 to 2.5, for a period of 10 seconds to 5 minutes at a temperature of from 20° C. to 90° C. At this pH, the chromic acid step is probably better characterized as a strong acid etching step, such as is customarily performed to roughen the surface prior to the oxide step.

U.S. Patent No. 4,717,439, which is herein incorporated by reference, describes a post-oxide process for reducing pink ring problems by treating a copper-oxide coating with an aqueous solution of an amphoteric element which forms an acidic oxide, such as selenium, tellurium or sulphur, at a preferred pH below about 5. This treatment is said to promote "leach-resistance," of the laminates by replacing the copper oxide with a copper selenide compound, thereby reducing pink-ring problems.

Several post-oxide treatments involve the chemical reduction of copper oxide, either to metallic copper, or to cuprous oxide. For example, related U.S. Patents No. 4,997,516 and 4,997,722 describe the difficulty of controlling the reduction of the copper oxide to improve bonding between the copper and polymeric layers. The approach of these patents is to carry out the reduction in the presence of a large molecular weight polymer. This approach is claimed to reduce pink-ring problems, by substantially reducing the copper oxide to metallic copper.

U.S. Patent No. 4,642,161 teaches a method of bonding a layer of copper to a layer of polymer wherein the surface of the layer of copper is first oxidized to cupric oxide, then reduced to metallic copper prior to bonding. It recognizes that the disclosure of the alkaline reduction post-oxide treatment in Japanese Patent Laid-Open No. 153797/1981 (the "797" patent), teaches the reduction of cupric oxide to cuprous oxide.

U.S. Patent No. 5,006,200, which is incorporated by reference herein, also suggests that bond strength is greater between cuprous oxide and the polymeric material than between cupric oxide and the polymeric material. The '200 patent teaches the reduction of cupric oxide to cuprous oxide without metallization by using an alkaline reducing solution

of between pH 7 and 12 in a temperature range of between 20° and 35° C, in a carefully controlled, continuously circulating reaction, to reduce pink-ring problems. The purpose of this alkaline reduction is to form a network of adhesion, between the copper atoms of the copper layer and the carbon atoms of the polymer layer via the oxygen atoms of the cuprous oxide, to act as a bridge between the copper and the carbon.

A problem with the methods that reduce the cupric oxide to either cuprous oxide or metallic copper is that the chemically reduced cuprous oxide or copper metal tends to reoxidize to cupric oxide after only a few days of contact with atmospheric oxygen, or as a result of baking to dry the reduced layer prior to bonding to a polymer. Hence, reduced copper oxide is best laminated immediately after formation.

It is an object of this invention to provide a process for bonding copper and a polymeric material that is less susceptible to the pink ring defect.

It is a further object of the present invention to provide a process for forming a copper/polymer bond that is resistant to pink ring and that does not require the chemical reduction of oxidized copper.

It is a further object of the present invention to provide a process for forming a copper/polymer bond that does not mask pink ring and that does not require an oxidizing acid, such as chromic, nor a highly acidic pH (i.e., 2.5).

SUMMARY OF THE INVENTION

This invention is directed to a process for bonding a layer of copper or a copper alloy to a layer of polymeric material, the process comprising the steps of:

(a) oxidizing the surface of a layer of copper or copper alloys with an oxidizing solution to form an oxide coating on the surface;

(b) subjecting the oxide coating on the layer of copper or copper alloy to an acidic solution to remove an amount of the oxide coating effective to enhance bonding with a polymeric material, the acidic solution characterized by having a pH of between 3.0 to 5.5, more preferably between 3.0 to 4.0; and

(c) bonding the layer of copper or copper alloy from step (b) to a polymeric material.

DETAILED DESCRIPTION OF THE INVENTION

This invention is directed to a process for bonding a layer of copper or a copper alloy to a layer of polymeric material, the process comprising the steps of:

(a) oxidizing the surface of a layer of copper or copper alloys with an oxidizing solution to form an oxide coating on the surface;

(b) subjecting the oxide coating on the layer of copper or copper alloy to an acidic solution to remove an amount of the oxide coating effective to enhance bonding with a polymeric material, the acidic solution characterized by having a pH of between 3.0 to 5.5, more preferably between 3.0 to 4.0; and

(c) bonding the layer of copper or copper alloy from step (b) to a polymeric material.

Oxidizing the surface of a layer of copper or copper alloy to form an oxide coating on the surface may be achieved by any suitable means that achieves a brown, dark brown or black oxide coating. The formation of brown, dark brown and black copper oxide coatings is well known in the art. For example, a brown oxide is produced by the method described in U.S. Patent No. 4,409,037, or is commercially available from Electrochemicals, Youngstown, Ohio as their No. 499 or preferably 501 oxide treatments. A conventional black oxide treatment comprises immersing the exposed layered copper or copper alloy in heated alkaline bath containing an oxidant such as an alkali metal chlorite, such as are described in U.S. Patent No. 4,717,439, or as is described in Example 1, infra.

It has been generally believed that a heavy, black copper oxide treatment of copper foil is more susceptible to oxide failure, evidenced by the pink ring defect. The bond strength of heavy, black copper oxide and dielectric is lower than industry

standards. Heavy, black copper oxide processed using the post oxide treatment of this invention has increased bond strength and avoids mechanical fracture at the copper/polymer interface. Table 1 reflects various acid and acid/salt combinations. In these examples the thickness of the initial oxide layer that was subject to the acid ranged from .3 mg/cm^2 to .7 mg/cm^2.

The second step of the present invention is subjecting the oxide coating on the layer of copper or copper alloy to an acidic solution, to remove an amount of the oxide coating effective to provide enhanced bonding with a layer of polymeric material. As those in the art would appreciate, in going from one reagent step to another, a rinse is performed to prevent contamination of the second reagent with the first. The temperature, pH, and time of exposure to the acid solution will depend upon the thickness of the oxide coating being treated. The pH may range from 3.0 to 5.5, while temperature may range from ambient to about 160° F. For example, an oxide coating having an initial thickness of about .3 mg/cm^2 is subjected to an acidic solution having a pH of about 3.0 - 4.0, at a temperature of about 130°F, for about 4 minutes. The acid solution in this pH range preferably comprises aqueous citric acid and trisodium phosphate in combination.

The acidic solution of the second step is an aqueous or substantially aqueous solution. The treatment of the oxide coating with an acidic solution may be performed by a solution that contains one or more mineral acids. Examples of mineral acids are sulfuric acid, hydrochloric acid, and phosphoric acid, preferably phosphoric. Optionally, the acids solution may contain one or more organic or inorganic salts. Examples of organic salts include the salts of mineral acids such as sodium sulfate, sodium chloride, sodium

phosphate, and potassium chloride. Preferably, the acidic solution contains a mixture of one or more organic acids and one or more of their water soluble salts. Examples of organic acids are oxalic, malonic, succinic, acetic, formic, propionic, butyric, citric, tartaric, phthalic and the like. The buffer solution would preferably contain one or more sodium, potassium, or lithium salts of one or more organic acids. Examples of salts of organic acids are sodium oxalate, sodium acetate, sodium formate, sodium citrate, sodium potassium tartrate, and sodium phthalate. A particularly preferred acidic solution is aqueous sodium acetate and acetic acid; however, its odor tends to make it somewhat disagreeable unless adequate ventilation is employed. Other suitable combinations include citric acid with sodium citrate and oxalic acid with sodium oxalate.

The step of bonding the copper to polymeric material is performed after the oxide coating has been treated with the buffer. The copper clad substrates are dried and bonded by lamination to dielectric prepreg bonding sheets, as is known by those skilled in the art. The step of bonding the layer of copper or copper alloy to a polymeric material may be performed in any manner consistent with the polymeric resins and equipment available to the processor. Such bonding methods include those described in U.S. patent No. 4,775,444 incorporated herein by reference.

Tables 1 reflects the duration of exposure, temperature of the bath and pH of various buffer solutions that were tested. As is understood by those skilled in the art, as the pH drops or the temperature rises, more oxide tends to be removed. The oxide panels were evaluated, following treatment as noted, for a change in color from the original black to various shades of brown as an indication

that an effective amount of oxide had been removed.

In Table 1, the treated panels were subjected to a "tape test". U.S. Patent No. 4,643,793 describes a method of testing for adhesion between copper surfaces and polymers, called a "tape test," in which adhesive tape is applied to the copper surface, then peeled off gradually. Upon peeling the tape, the surfaces of the treated panels were evaluated both for transfer of the adhesive to the surface of the panel, and for the transfer of oxide to the adhesive by the appearance of oxide residue on the tape. The most favorable result was a positive adhesive transfer with no oxide transfer. However, in practice, even those panels which allow some oxide transfer work reasonably well in minimizing "pink ring", notwithstanding their apparently lower adhesion strength.

Table 1 compares the tape test results for various acid solutions of the invention and others as a function of pH, and temperature. The data suggests that the temperature of the acid solution of this invention and the time of immersion control the amount of oxide removed, and ultimately the result on the tape transfer. The best "tape test" results occurred for sodium acetate/acetic acid solutions having a pH ranging between 3.8 - 4.3 (entries 20 - 28) wherein the temperature ranged from ambient to 110°. For acetic acid/sodium acetate solutions at ambient temperature, variations in immersion time from 3 - 10 minutes had little effect. However, at higher temperatures (see entries 24 and 25), the lighter color of the treated panel (brown and light brown) respectively) indicated that a greater thickness of oxide had been removed.

A comparison was made for the "pink ring" defect between circuit boards produced by the method for the present invention and circuit boards

TABLE 1
EFFECT OF ACID COMPOSITION ON THE TAPE TEST

						Tape Test	
Chemical	*Conc. (g/L)*	*Time (Min)*	*Temp (Degrees F)*	*pH*	*Color (After Post Dip)*	*Adhesive Transfer*	*Oxide Transfer*
1) Trisodium Phosphate Phosphoric Acid pH adjust	50 -	7	Ambient	3.5	Dark Brown	Yes	Yes
2) Trisodium Phosphate Phosphoric Acid pH adjust	50 -	2	Ambient	2.0	Brown	No	Yes
3) Trisodium Phosphate Hypophosphorus Acid pH adjust	25	4	130	5.0	Silver/Black	Yes	Slight
4) Sodium Citrate Sulfuric pH adjust	30	4	130	4.0	Brown	No	Yes
5) Trisodium Phosphate Citric Acid Sulfuric pH adjust	19.9 6.5 -	4	130	5.0	Light Brown	Yes	No
6) Citric Acid	6.5	4	Ambient	2.3	Black	Yes	Slight

TABLE 1

EFFECT OF ACID COMPOSITION ON THE TAPE TEST (cont'd.)

Chemical	Conc. (g/L)	Time (Min)	Temp (Degrees F)	pH	Color (After Post Dip)	Tape Test Adhesive Transfer	Tape Test Oxide Transfer
7) Citric Acid	6.5	4	130	2.3	Brown	No	Yes
8) Citric Acid Trisodium Phosphate	6.5 18.7	4	Ambient	6.5	Black	Slight	Yes
9) Citric Acid Trisodium Phosphate	6.5 18.7	4	130	6.5	Dark Pink	Slight	No
10) Citric Acid Monosodium Phosphate	6.5 18.7	4	Ambient	3.0	Black	Yes	Slight
11) Citric Acid Monosodium Phosphate	6.5 18.7	4	130	3.0	Grey/Black	No	Yes
12) Citric Acid Trisodium Phosphate	6.5 18.7	4	Ambient	6.5	Black	Yes	Slight
13) Citric Acid Trisodium Phosphate Sulfuric pH adjust	6.5 18.7 -	4	Ambient	5.0	Black	Yes	Slight

TABLE 1
EFFECT OF ACID COMPOSITION ON THE TAPE TEST (cont'd.)

Chemical	*Conc. (g/L)*	*Time (Min)*	*Temp (Degrees F)*	*pH*	*Color (After Post Dip)*	*Tape Test* *Adhesive Transfer*	*Tape Test* *Oxide Transfer*
14) Citric Acid Trisodium Phosphate Sulfuric pH adjust	6.5 18.7 -	4	100	5.0	Dark Brown	No	Yes
15) Citric Acid Trisodium Phosphate Sulfuric pH adjust	6.5 18.7 -	4	110	5.0	Brown	No	Yes
16) Citric Acid Trisodium Phosphate Sulfuric pH adjust	6.5 18.7 -	4	120	5.0	Light Brown	Yes	No
17) Citric Acid Trisodium Phosphate Sulfuric pH adjust	6.5 18.7 -	4	130	5.0	Dark Pink	Yes	No
18) Sodium Sulfate Sulfuric pH adjust	50 -	6	Ambient	3.5	Dark Brown	No	Yes
19) Sodium Sulfate Sulfuric pH adjust	50 -	2	Ambient	2.0	Brown	No	Yes
20) Sodium Acetate Acetic Acid	0.5M (68g/L) 0.5M (30g/L)	4	Ambient	4.3	Black	Yes	No

TABLE 1
EFFECT OF ACID COMPOSITION ON THE TAPE TEST (Cont'd.)

Chemical	Conc. (g/L)	Time (Min)	Temp (Degrees F)	pH	Color (After Post Dip)	Tape Test: Adhesive Transfer	Tape Test: Oxide Transfer
21) Sodium Acetate Acetic Acid	0.5M 0.5M	10	Ambient	4.3	Dark Brown	Yes	Slight
22) Sodium Acetate Acetic Acid	0.5M 0.5M	4	100	4.3	Black	Yes	Slight
23) Sodium Acetate Acetic Acid	0.5M 0.5M	4	110	4.3	Dark Brown	Yes	Slight
24) Sodium Acetate Acetic Acid	0.5M 0.5M	4	120	4.3	Brown	Slight	Yes
25) Sodium Acetate Acetic Acid	0.5M 0.5M	4	130	4.3	Light Brown	Slight	Yes
26) Sodium Acetate Acetic Acid	40 88 ml/l	3	Ambient	3.8	Dark Brn./Black	Yes	No
27) Sodium Acetate Acetic Acid	40 88 ml/l	5	Ambient	3.8	Dark Brn./Black	Yes	No
28) Sodium Acetate Acetic Acid	40 88 ml/l	10	Ambient	3.8	Dark Brown	Yes	No

TABLE 2
TIME OF POST DIP v. TEMPERATURE FOR OXIDE OF EXAMPLE 1

			Remaining Oxide Weight		Tape Test	
pH	*Temp*	*Time (Min.)*	*(MG/CM²)*	*Color*	*Adhesive Transfer*	*Oxide Transfer*
3.88	110° F	2	0.20	Dark Brown	Yes	Yes
		3	0.22	Dark Brown	No	Yes
		4	0.14	Brown	Yes	Yes
		5	0.15	Brown	No	Yes
	120° F	2	0.21	Dark Brown	Yes	Yes
		3	0.11	Brown	Slight	Yes
		4	0.12	Light Brown	No	Yes
		5	0.02	Pink	No	Yes

[1] Acetic/Acetate .32 mL/L acetic acid
.66 g/L sodium acetate

TABLE 2
TIME OF POST DIP v. TEMPERATURE FOR OXIDE OF EXAMPLE 1 (cont'd.)

pH	Temp	Time (Min.)	Remaining Oxide Weight (MG/CM^2)	Color	Tape Test: Adhesive Transfer	Tape Test: Oxide Transfer
4.0	110° F	2	0.22	Dark Brown	No	Yes
		3	0.11	Light Brown	No	Yes
		4	0.11	Light Brown	No	Yes
		5	0.03	Dark Pink	No	Yes
	120° F	2	0.16	Brown	No	Yes
		3	0.14	Brown	No	Yes
		4	0.05	Light Brown	No	Yes
		5	0.01	Pink	Yes	No

[2] Citric/Phosphate 17 g/L Citric acid
18.7 g/L Trisodium phosphate

TABLE 2
TIME OF POST DIP v. TEMPERATURE FOR OXIDE OF EXAMPLE 1 (cont'd.)

					Tape Test	
pH	*Temp*	*Time (Min.)*	*Remaining Oxide Weight (MG/CM^2)*	*Color*	*Adhesive Transfer*	*Oxide Transfer*
5.0	110° F	2	0.25	Dark Brown	No	Yes
		3	0.15	Brown	No	Yes
		4	0.20	Brown	No	Yes
		5	0.12	Brown	No	Yes
	120° F	2	0.14	Dark Brown	No	Yes
		3	0.06	Light Brown	Yes	Slight
		4	0.05	Light Brown	Yes	No
		5	0.04	Light Brown	Yes	No

[3] Citric/Phosphate: 6.5 g/L citric acid; 18.7 g/L trisodium phosphate; pH adjust with Sulfuric acid.

produced by the substantially identical method except that the latter method did not employ the acid solution of the present invention. The first acid solution comprised an aqueous solution containing 16 g/L citric acid, 18 g/L trisodium phosphate and having pH 4.1. Copper panels that were oxidized according to the method of Example 1 were separated into two sets. The first set was immersed in the above described acidic solution for 4 minutes at 120° F and then rinsed. Both sets of boards were dried by baking and then bonded to a polymer material. The resulting boards were drilled with through holes and then electrolessly plated using conventional techniques. When the polymeric material was ground away to reveal the oxide layer on both sets of boards, the oxide layer on the second set exhibited "pink ring" of 12 - 15 mils radius around 50% of the through holes. In contrast, boards that were processed by the method of the present invention exhibited no significant "pink ring."

A second comparison was made using an aqueous acidic solution comprised of 88 ml/L acetic acid, 40 g/L sodium acetate, with a pH of 3.2. The oxide samples were subjected to this solution for 3 minutes at 130° F. The boards that were not processed through the post oxide acid solution of step (b) were inspected and revealed significant "pink ring" around 30 - 35% of the panel's through holes. In contrast, the boards that were produced by the method of the present invention exhibited "pink ring" around only five holes out of 100,000, i.e., .005%.

Table 2 provides additional tape test results for three acidic compositions as a function of time and temperature.

In the examples that follow, Example 7 is the preferred acid treatment for the thick black oxide of Example 6.

EXAMPLE 1

The surface of a copper layer was oxidized to a black oxide by dipping it for six minutes in a solution at 165° F and comprising 72 g/L sodium chlorite, 25 g/L NaOH, and 12.5 g/L trisodium phosphate dodecahydrate. After the dip, the copper layer was removed and subjected to a running water rinse for two minutes. A black oxide coating of about 0.4 mg/cm^2 resulted.

EXAMPLE 2

Copper clad laminate was coated with an oxide according to Example 1. The copper clad laminate with the oxide coating was immersed in a solution of 16.0 g/L citric acid and 18 g/L trisodium phosphate, pH 4.1, for 4 minutes, at 110° F.

EXAMPLE 3

Copper clad laminate was coated with oxide according to Example 1. The copper clad laminate with the oxide treatment were immersed in a solution of 6.5 g/L citric acid and 18.7 g/L trisodium phosphate, pH adjusted to 5.0 using sulfuric acid, for 3 minutes, at 120°F.

EXAMPLE 4

Copper clad laminate was coated with oxide according to Example 1. The copper clad laminate with the oxide treatment were immersed in a solution of 0.5M acetic acid and 0.5M sodium acetate, pH 4.3, for 4 minutes, at 120°F.

EXAMPLE 5

Copper clad laminate was coated with oxide according to Example 1. The copper clad laminate with the oxide treatment were immersed in a solution of 10.2 g/L potassium hydrogen phthalate and 22.3 ml/L of 1.0 M HCl, pH 3.0, for 5 minutes, at ambient temperature.

EXAMPLE 6

The surface of a copper layer was oxidized to a black oxide by immersing it for 7 minutes in a solution at 175°F that contained 93 g/L sodium chlorite, 48 g/L sodium hydroxide, and 1 g/L trisodium phosphate dodecahydrate. After the oxidation, the copper layer was removed and subjected to a running water rinse for 2 minutes. A black oxide coating of about 0.64 - 0.66 mg/cm^2 resulted.

EXAMPLE 7

Copper clad laminate was coated with an oxide according to Example 6. The copper clad laminate with the oxide treatment was immersed in a solution of 20 g/L citric acid and 7.5 g/L trisodium phosphate dodecahydrate at pH 3.0, for 8 minutes at 120°F.

WHAT IS CLAIMED IS:

1. An improved process for bonding a layer of copper or copper alloy to a layer of a polymeric material, the process comprising the steps of:

(a) oxidizing the surface of a layer of copper or copper alloy with an oxidizing solution to form an oxide coating on the surface;

(b) subjecting the oxide coating on said layer of copper or copper alloy to an acidic solution having a pH from between 3.0 to 5.5 to remove an amount of the oxide coating effective to enhance bonding with a polymeric material; and

(c) bonding the layer of copper or copper alloy from step(b) to a polymeric material.

2. The process of claim 1, wherein the acidic solution has a pH of 3.0 to 4.0.

3. The process of claim 1, wherein the acidic solution is buffered.

4. The process of claim 1, wherein the oxide coating of Step (a) is from about .3 mg/cm^2 to about .7 mg/cm^2.

5. The process of claim 1, 2, 3, or 4 wherein the acidic solution comprises one or more members of the group of acids consisting of oxalic, acetic, formic, citric, tartaric and phthalic and their respective water soluble salts including the alkali metal salts sodium, potassium, lithium and the like.

6. The process of claim 1, wherein the acidic solution comprises citric acid and a sodium phosphate.

7. The process of claim 1, wherein the acidic solution comprises citric acid and trisodium phosphate.

8. The process of claim 7, wherein the pH of the buffer is adjusted with a mineral acid.

9. The process of claim 1, wherein the acidic solution comprises acetic acid and sodium acetate.

10. The process of claim 9, wherein the acidic solution has a pH within the range of about 3.8 to 4.3.

11. The process of claim 1, wherein the acidic solution comprises phthalic acid and potassium phthalate.

12. The process of claim 1, wherein the acidic solution comprises citric acid and sodium citrate.

13. The process of claim 1, wherein the acidic solution comprise oxalic acid and sodium oxalate.

14. In a method of bonding a layer of copper having a copper oxide coating to a polymeric material in a printed circuit board laminate, the improvement comprising subjecting the oxide coating to an acidic solution to remove an amount of the oxide coating effective to enhance bonding with a polymeric material, the acidic solution having a pH in a range between 3.0 to 5.5.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/08777

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 H05K3/38

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	H05K ; C23C ; C23G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
E	US,A,5 106 454 (GEORGE R. ALLARDYCE ET AL.) 21 April 1992 see column 2, line 15 - line 46 see column 2, line 55 - column 3, line 66 see column 3, line 29 - column 5, line 47 see claims 1-9,19-39	1,5
A		2,3,14

A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 563 (M-1058)14 December 1990 & JP,A,2 238 942 (MISTUBISCHI ELECTRIC CORP.) 21 September 1990 see abstract	1-3,5,14

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
03 JUNE 1992	26. 06. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	GOOSSENS A.

1

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9108777 SA 57362

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 03/06/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5106454		None	

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82